

Study of molecular interactions in binary mixtures of acetophenone derivative and cyclohexylamine

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Abstract : Dielectric constant of cyclohexylamine (CHA) + acetophenone (ACT) and CHA + p-chloroacetophenone (PCLA) mixtures has been measured at 100 KHz at 30°C. The Kirkwood correlation factor g_{eff} and g_{H} , excess thermodynamic functions and excess polarization of mixing have been calculated. The values of correlation factors in the mixture remain above unity, which indicated the predominance of microheterogeneous cluster with parallel or cooperative angular correlation (α -cluster). The dipolar contribution of excess free energy of mixing, arising from long-range electrostatic interaction and short-range interaction between identical molecules and short-range interaction between dissimilar molecules, has been calculated separately. For both the systems, the excess viscosity exhibits negative deviation due to hydrogen bonded effects and dipolar interaction.

Keywords : Dielectric constant, Kirkwood correlation factor, free energy, long-range and short-range interaction.

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1. Introduction

The Onsager-Kirkwood theory [1] of dielectric polarization of polar liquid can be applied to the mixture of polar liquid. It is fairly clear that hindered rotation does play an important role in the dielectric polarization of polar liquids. The hindered relative rotation of a pair of neighbouring molecules may be due to electrostatic dipole-dipole coupling and impact to other intermolecular forces, van der Waals forces and repulsive forces determining the molecular shape. The linear correlation factor (g), whose values differing from unity, is a measure of hindering effect of a molecule on its neighbour. This parameter is a direct measure of the extent and nature of molecular association. Study of g and of excess thermodynamic functions of mixing of a mixture, therefore, gives useful information regarding the dipole interaction between the molecules in a mixture [2-4]. Likewise, the experimental determination of mutual correlation factor and excess

thermodynamical function of mixing could be used to interpret structural composition in binary mixture of polar liquids.

Authors have earlier [5-7] investigated the dielectric relaxation studies of acetophenone and amine mixtures in dilute solutions of non-polar solvents, and found the formation of complexes on the basis of hydrogen bonding between these molecules. It is generally observed that hydrogen bond is a strong intermolecular interaction, which causes a significant effect upon the structure, thermodynamic properties and macroscopic dielectric properties of the solution of polar liquids.

Sutherland *et al* [8] developed a relation for the excess thermodynamical functions of mixing based on the exact solution of the mean spherical model (MSM) [9] for simple polar mixture proposed by Adelman and Deutch [10]. Winkelmann and Quitzsch [11] further extended the dipolar theory of binary mixtures to link with the known

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dipolar theories of thermodynamic function [8]. Swain [12,13] studied the excess thermodynamic function in binary mixture taking associated and non-associated liquids. Literature survey shows that attempts have not, so far, been made to investigate the different dielectric parameters and thermodynamical parameters in the binary mixtures of ACT+CHA and PCLA+CHA. In view of this, it is of great interest to investigate mutual correlation functions in the binary mixture of CHA with ACT and PCLA and the dipolar thermodynamic excess function of mixing due to (i) long range electrostatic interaction, (ii) short range interaction between identical molecules and (iii) short range interaction between dissimilar molecules.

2. Theory

The Kirkwood correlation factor g [1] explains the orientation of the electric dipoles in the polar liquids and it is given by the equation,

$$\frac{4\pi N \mu^2 \rho}{9KT} g = \frac{(\epsilon_{or} - \epsilon_{\infty r})(2\epsilon_{or} + \epsilon_{\infty r})}{\epsilon_{or}(\epsilon_{\infty r} + 2)^2} \quad (1)$$

The two modified forms of the above equation, normally used to study the orientation of the electric dipoles in the binary mixture [2,3], are defined by

$$\frac{4\pi N}{9KT} \left(\frac{\mu_r^2 \rho_r}{M_r} f_r \right) g_{eff} = \frac{(\epsilon_m - \epsilon_{\infty m})(2\epsilon_m + \epsilon_{\infty m})}{\epsilon_m(\epsilon_{\infty m} + 2)^2} \quad (2)$$

where g_{eff} is Kirkwood factor for a binary mixture, $f_{r=a,b}$ represent the mole fraction of two molecules respectively. $\epsilon_{\infty m}$ is the square of the refractive index of the mixture. M_r is corresponding molecular weight. The second form is

$$\frac{4\pi N}{9KT} \left(\frac{\mu_r^2 \rho_r g_r}{M} f_r \right) g_f = \frac{(\epsilon_m - \epsilon_{\infty m})(2\epsilon_m + \epsilon_{\infty m})}{\epsilon_m(\epsilon_{\infty m} + 2)^2},$$

where g_r represents the Kirkwood correlation factor of pure two liquids a and b respectively and are assumed to be affected by an amount g_f in the mixture. The value of g_f is unity for an ideal liquid and deviation from unity may indicate interaction between two components in the mixture.

The molar polarization of the binary mixture utilizing the separation of total correlation and incorporating Onsager's [11] reaction field factor, is given by

$$P_m = \frac{4\pi N \epsilon_m}{\epsilon_m + 2} \left[\sum_{r=a,b} \frac{(\epsilon_{\infty r} - 1)}{(2\epsilon_m + \epsilon_{\infty r})} f_r \alpha_r + \sum_{a,b} \left(\frac{\epsilon_{\infty r} + 2}{2\epsilon_m + \epsilon_{\infty r}} \right)^2 \frac{(2\epsilon_m + 1) f_r \mu_r^2 g_{rr}}{9kT} + \frac{(\epsilon_{\infty a} + 2)(\epsilon_{\infty b} + 2)(2\epsilon_m + 1)}{(2\epsilon_m + \epsilon_{\infty a})(2\epsilon_m + \epsilon_{\infty b})} \frac{\mu_a \mu_b}{9kT} (g_{ab} - 1) \right], \quad (3)$$

where subscripts a and b refer to the molecules of variety a and b , α_r the polarizability of the respective component, N the Avogadro's number, k Boltzmann's constant, T temperature (K), μ_r the dipole moment of the component, ϵ_m the dielectric constant of the mixture, $\epsilon_{\infty r}$ is the square of the refractive index of the components, g_{rr} represents the linear correlation factor between identical molecules $a-a$ or $b-b$ and g_{ab} denotes the mutual correlation factor between the dissimilar molecules $a-b$.

The excess polarization is given by

$$\Delta P_m = P_m - (P_1 f_1 + P_2 f_2), \quad (4)$$

where P_1 and P_2 are the molar polarization of the components. Excess dielectric constant $\Delta\epsilon_0$ and excess viscosity $\Delta\eta$ have also been calculated in the similar manner.

The excess Helmholtz free energy ΔF , which is almost equal to the excess Gibbs free energy ΔG for a matter in condensed phase, is given as [11]

$$\begin{aligned} \Delta F = & -\frac{N}{2} \sum_{r=a,b} f_r \mu_r^2 (R_{fr} - R_{fr0}) \\ & \sum_{r=a,b} f_r^2 \mu_r^2 (g_{rr} - 1) (R_{fr} - R_{fr0}) \\ & + f_a f_b \mu_a \mu_b (g_{ab} - 1) (R_{fa} + R_{fb} - R_{fa0} - R_{fb0}) \\ = & \Delta F_0 + \Delta F_{rr} + \Delta F_{ab}. \end{aligned} \quad (5)$$

The first term ΔF_0 in eq. (5) represents the excess dipolar energy due to long range electrostatic interaction; the second term ΔF_{rr} gives the excess dipolar energy due to short-range interaction between identical molecules and the third term ΔF_{ab} gives the excess dipolar energy due to short-range interaction between dissimilar molecules.

The terms R_{fr0} and R_{fr} which give the reaction field parameters in the pure liquid and in the mixture respectively, are given by

$$R_{fro} = \frac{8\pi N}{9V_r} \frac{(\epsilon_{or} - 1)(\epsilon_{\infty r} + 2)}{(2\epsilon_{or} + \epsilon_{\infty r})}, \quad (6a)$$

$$R_{fr} = \frac{8\pi N}{9V_r} \frac{(\epsilon_m - 1)(\epsilon_{\infty r} + 2)}{(2\epsilon_m + \epsilon_{\infty r})}, \quad (6b)$$

where V_r is the molar volume of the components and ϵ_{or} the dielectric constant of the pure liquids.

3. Methods of measurement

Compounds used in the present study of AR grade were all procured from BDH, India. The dielectric constant (ϵ_0) at 100 KHz was measured using a dipole meter by directly measuring the capacitance and calibrating it for standard liquids. The dielectric constant (ϵ_∞) at optical frequency was obtained by squaring the refractive index for sodium D-lines, measured with the help of an Abbe's refractometer. The accuracy of measurements of ϵ_0 , ϵ_∞ , viscosity, density and temperature are nearly 0.1%, 0.03%, 0.1%, 0.001% and $\pm 0.5^\circ\text{C}$, respectively. The density and viscosity measurement were made with the help of a pycnometer and Ostwald viscometer respectively. All measurements were made at constant temperature 303 K.

Table 1. Values of ϵ_0 , ϵ_∞ , density (d), viscosity (η), g_{eff} , g_f and P_m .

Mole fraction of 1st compound	ϵ_0	ϵ_∞	d (gm/cc)	η (cp)	g_{eff}	g_f	P_m (cc)
PCLA + CHA							
0	4.850	2.137	0.864	0.880	0.999	1.000	65.66
0.00888	5.050	2.144	0.865	0.918	1.048	1.036	67.17
0.07523	8.175	2.164	0.885	0.920	1.846	1.685	83.05
0.11191	10.175	2.179	0.902	0.870	2.285	2.011	89.12
0.18779	12.975	2.199	0.931	0.868	2.750	2.270	95.35
0.25921	14.700	2.223	0.955	0.886	2.904	2.283	98.57
0.38843	15.950	2.259	0.997	0.941	2.770	2.034	101.46
0.49233	16.550	2.294	1.032	0.980	2.560	1.829	103.23
0.62792	16.650	2.330	1.078	1.029	2.320	1.562	104.80
0.74491	16.775	2.367	1.108	1.073	2.118	1.383	106.20
0.82547	16.625	2.390	1.137	1.169	1.968	1.263	106.91
0.91197	16.475	2.398	1.173	1.201	1.841	1.161	107.67
1.0000	15.450	2.421	1.186	1.240	1.610	1.000	107.38
ACT + CHA							
0	4.850	2.137	0.864	0.880	0.999	1.000	65.66
0.03858	6.775	2.148	0.863	0.824	1.427	1.414	76.88
0.07463	9.225	2.156	0.878	0.791	1.892	1.862	85.60
0.11787	14.250	2.185	0.881	0.803	2.754	2.691	95.25
0.19680	14.750	2.189	0.893	0.738	2.401	2.325	95.91
0.27364	16.125	2.200	0.908	0.733	2.281	2.194	97.49
0.39566	16.625	2.226	0.928	0.726	1.919	1.832	98.02
0.51701	16.875	2.252	0.946	0.725	1.639	1.556	98.28
0.63516	16.975	2.281	0.963	0.713	1.421	1.344	98.38
0.75731	17.075	2.307	0.987	0.719	1.248	1.177	98.48
1.0000	17.390	2.355	1.020	0.733	1.065	1.000	98.79

4. Results and discussion

The plots of excess dielectric constant $\Delta\epsilon_0$ versus % mole fraction of ACT and its derivatives are shown in Figure 1. The $\Delta\epsilon_0$ is found to be positive over the entire range of concentration representing the formation of complex and found to be maximum near 10% of ACT and 25% of PCLA in the mixture. The values of g_{eff} and g_f for various composition of the mixture are given in Table 1. The dipole moment of ACT, PCLA and CHA are taken to be 3.01D, 2.40D and 1.68D respectively [14].

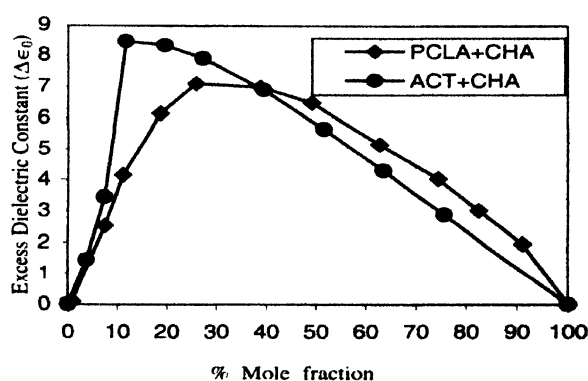


Figure 1. Variation of excess dielectric constant ($\Delta\epsilon_0$) with % mole fraction of ACT and its derivative.

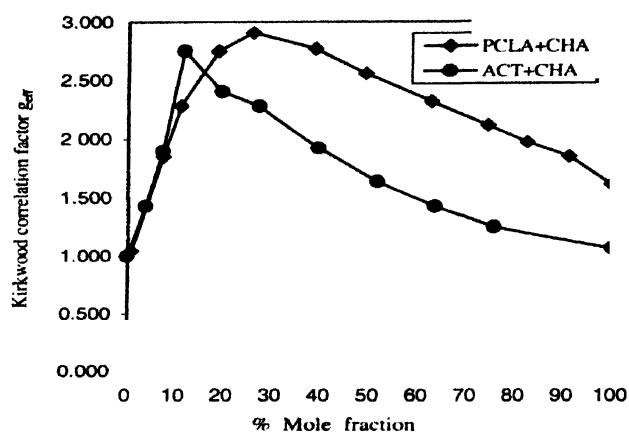


Figure 2. Variation of Kirkwood correlation factor (g_{eff}) with % mole fraction of ACT and its derivative.

From Table 1 and Figure 2, it is observed that the g_{eff} values for the mixture are greater than unity and deviation from unity is maximum at 10% of ACT and 25% of PCLA indicating stronger interaction between two components. Similar results were obtained by Fattepur *et al* [15,16] for methanol + aniline and methanol + 4-ethyl phenol mixtures. This is also justified in the observation that $\Delta\epsilon_0$ is maximum around the same concentration of ACT and PCLA as shown in Figure 1. It is clear from Figure 2 that g_{eff} increases from unity at both ends and attains a maximum value in the mid-range and then drops to unity at other end. It is supposed that the two dissimilar molecules in the mixture form microheterogeneous cluster that vary in composition over the entire concentration range in both the mixture. The magnitude of g_{eff} reflects the arrangement of the dissimilar molecules in those clusters. When the dissimilar molecules align in the same direction (angular correlation is established) they are said to form α -multimers and value of g_{eff} comes out greater than 1. These results are in good agreement with the observation of Swain [17] in the binary mixture of associated-associated liquid-mixtures.

The values of molar polarization (P_m) and excess molar polarization (ΔP_m) are shown in Tables 1 and 2, respectively. The variation of excess molar polarization ΔP_m is depicted in Figure 3. It is observed that ΔP_m is positive and maxima occur nearly 10% of ACT and 25% of PCLA again confirms our earlier conclusion regarding the formation of complex in the system. It is clear from the table that molar polarization (P_m) follows the Kirkwood correlation factor g_{eff} with the variation of concentration. Maxima in (P_m) values are also found at the same concentration where these have been observed

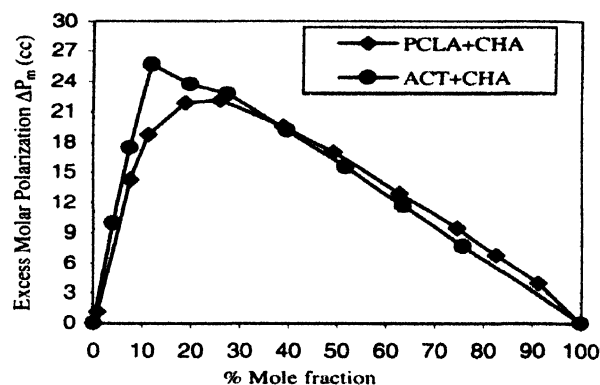


Figure 3. Variation of excess molar polarization (ΔP_m) with % mole fraction of ACT and its derivative.

in g_{eff} values. This shows that association in these molecules is stable. α -multimers are also supported by positive ΔP_m values. Similar results were obtained by Garabadu and Swain [18] for pentanol mixtures.

The excess free energy ΔF for mixtures is shown in Table 2 and the plots of ΔF are shown in Figure 4. It is

Table 2. Values of excess parameters ($\Delta\epsilon_0$, ΔP_m , ΔF_0 , ΔF_m , ΔF_{ab} and ΔF).

Mole fraction of 1st compound	$\Delta\epsilon_0$	ΔP_m (cc)	ΔF (J/Mole)	ΔF_0 (J/Mole)	ΔF_m (J/Mole)	ΔF_{ab} (J/Mole)
PCLA + CHA						
0	0	0	0	0	0	0
0.00888	0.106	1.14	-12.76	-13.11	0.75	0.27
0.07523	2.528	14.25	-199.19	-196.10	1.98	-5.08
0.11191	4.139	18.79	-303.63	-262.39	2.60	-43.85
0.18779	6.134	21.86	-462.04	-309.75	2.75	-155.03
0.25921	7.102	22.10	-567.30	-318.25	1.52	-250.57
0.38843	6.983	19.60	-604.81	-288.75	-1.60	-314.47
0.49233	6.481	17.03	-565.87	-257.85	-5.92	-302.10
0.62792	5.144	12.94	-453.44	-202.57	-10.60	-240.27
0.74491	4.029	9.46	-339.48	-156.42	-16.42	-166.64
0.82547	3.025	6.81	-244.34	-117.78	-18.05	-108.50
0.91197	1.958	3.96	-147.49	-76.00	-19.39	-52.09
1.0000	0	0	0	0	0	0
ACT + CHA						
0	0	0	0	0	0	0
0.03858	1.449	9.94	-105.36	-110.92	0.31	5.25
0.07463	3.454	17.47	-227.03	-214.25	0.59	-13.36
0.11787	8.446	25.69	-500.24	-355.87	0.55	-144.92
0.19680	8.321	23.73	-502.85	-319.34	0.77	-184.28
0.27364	7.898	22.76	-548.94	-314.33	0.66	-235.25
0.39566	6.893	19.25	-474.22	-265.29	0.69	-209.61
0.51701	5.645	15.49	-366.16	-212.36	0.69	-154.49
0.63516	4.287	11.68	-251.49	-157.24	0.76	-95.00
0.75731	2.880	7.73	-145.10	-101.23	0.77	-44.64
1.0000	0	0	0	0	0	0

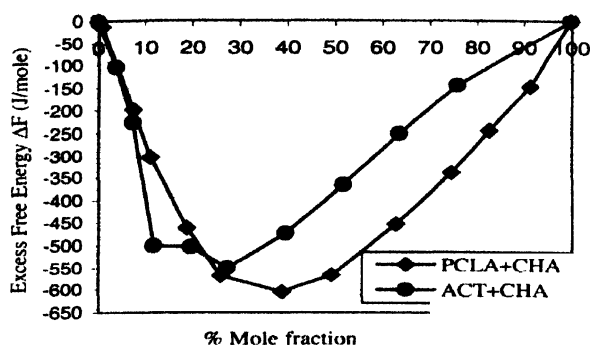


Figure 4. Variation of excess free energy (ΔF) with % mole fraction of ACT and its derivative.

observed that excess free energy ΔF for both the mixtures are negative. ΔF reflects the total picture taking into account the near (short) and far (long) range dipolar interaction between identical and dissimilar molecules. Negative values of ΔF corroborate our finding on g_{eff} and ΔP_m that there is formation of α -multimers in these systems. Figure 5 represents the variation of ΔF_{ab} for the mixtures under the present investigation. The values of

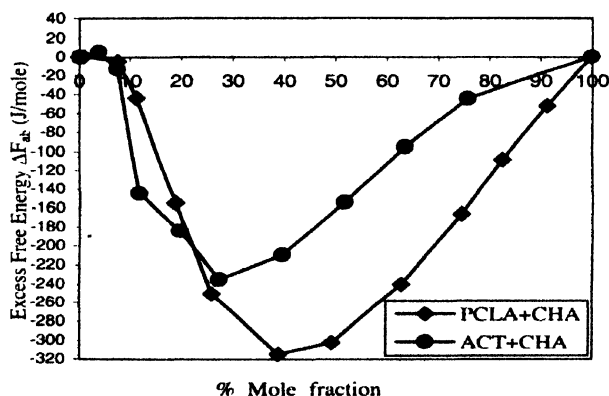


Figure 5. Variation of excess free energy (ΔF_{ab}) with % mole fraction of ACT and its derivative.

ΔF_{ab} are expected to remain negative for the mixtures for which $g_{eff} > 1$. This may be due to the facts that increase in internal energy of the system necessitated by the reinforcing of angular correlation between dissimilar molecules.

It is also observed from Table 2 that ΔF_{rr} remains positive over the entire range of ACT + CHA system but for PCA + CHA system, it changes from positive to negative on increasing the concentration of PCA in the mixture. This may be due to the fact that anti-parallel alignment dominates where CHA is in excess and parallel alignment is the dominant factor in the PCA-rich region. It is only when the short-range interaction between identical molecules alone is considered.

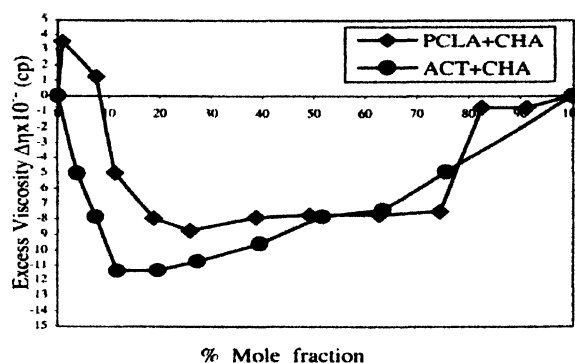


Figure 6. Variation of excess viscosity ($\Delta \eta$) with % mole fraction of ACT and its derivative.

The variation of excess viscosity ($\Delta \eta$) with concentration of ACT and PCA is shown in Figure 6. The negative deviation $\Delta \eta$ from linearity for both the systems indicates that dispersive forces are primarily responsible for the interaction [19]. In the present study, the interaction may be due to the formation of H-bonding between $-\text{COCH}_3$ group of ACT and CHA molecules and may also be due to chloro group of PCA and CHA molecules as shown in the Figures 7 and 8. Similar results were obtained by Govindan and Ravichandran

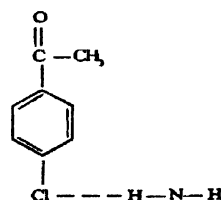


Figure 7. Molecular association through H-bonding in PCA + CHA system.

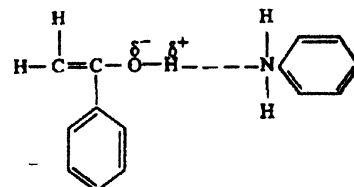


Figure 8. Molecular association through H-bonding in ACT + CHA system.

[19] for binary mixture of ethylmethyl ketone and alcohol molecules. The negative deviation of $\Delta \eta$ implies that the dipole interactions are more probable in these systems in addition to the intermolecular H-bonding. Similar behaviour was reported by Aminabhavi *et al* [20] for the binary mixture of bromoform with benzene, toluene and acetonitrile.

5. Conclusions

From the present work, following conclusions have been drawn.

- (i) Formation of complexes is found in both the systems.
- (ii) The presence of α -multimers is noticed in the systems under investigation.
- (iii) Long-range and short-range dipolar interactions and reinforcement of angular correlation between dissimilar molecules, were identified.
- (iv) H-bonding between $-\text{COCH}_3$ group of ACT and CHA was noticed. It is more stronger in PCLA than ACT due to chloro group.

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